

(21) Application No 8326605

(22) Date of filing

5 Oct 1983

(30) Priority data

(31) 8229498

(32) 15 Oct 1982

(33) United Kingdom (GB)

(43) Application published

2 May 1984

(51) INT CL<sup>3</sup> G01N 27/46

(52) Domestic classification

G1N 25A1 25C4C3

25C4D 25D6 BPX

U1S 1272 1466 1483

G1N

(56) Documents cited

None

(58) Field of search

G1N

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(54) Hydrogen concentration meter

face of the metal.

(57) A hydrogen concentration meter comprises.

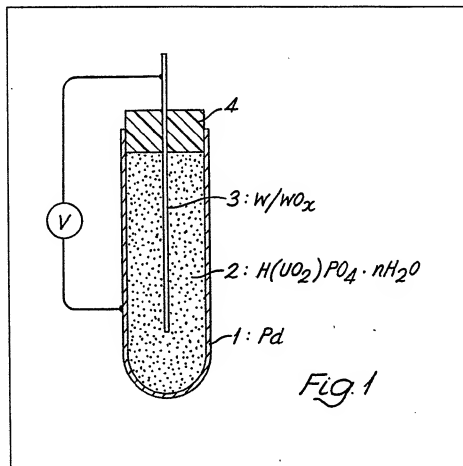
(i) a conductive component 1, exposable to hydrogen to be measured and in which hydrogen is soluble and mobile (e.g. of palladium),

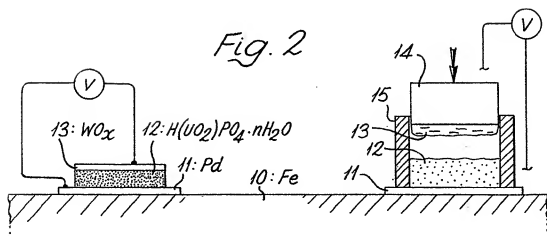
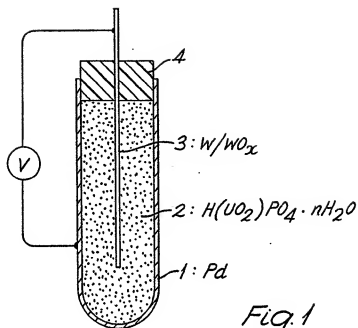
(ii) a reference electrode 3 which can reversibly accept hydrogen and which has been equilibrated with

(iii) a solid state electrolyte 2 for hydrogen cations.

The reference electrode may comprise tungsten defect hydrogen tungsten bronze and the electrolyte may be hydrogen uranyl phosphate although many other examples are given.

The cell shown is used for measurement in a gas. To measure hydrogen in a metal, layers (i), (ii) and (iii) may be formed directly on the





## SPECIFICATION

### Hydrogen concentration meter

- 5 This invention relates to a hydrogen concentration meter. Because hydrogen embrittles structural metals, especially steels, the detection and measurement of dissolved hydrogen in metal is an important endeavour. The detection of some parts per million of hydrogen in air can also be required on occasion.

According to the present invention, a hydrogen concentration meter comprises

- (i) a conductive component exposable to the hydrogen to be measured and in which hydrogen is soluble and mobile,  
 (ii) a reference electrode which can reversibly accept hydrogen, and  
 (iii) a solid-state electrolyte for hydrogen cations connecting the component (i) with the reference electrode (ii), the said component and reference electrode being connectable to opposite sides of a voltmeter, characterised in that the reference electrode (ii) has an inherent hydrogen activity and reaches a hydrogen-concentration equilibrium with the electrolyte (iii).

- Preferably the electrolyte (iii) is one of phosphomolybdic acid, phosphotungstic acid, zirconium hydrogen phosphate, partially hydrated zirconia, hydrated hydrogen uranyl phosphate/arsenate/periodate, perfluorocarbon sulphonic acid,  $\beta$ -alumina (which may be hydronium-substituted), hydrogen- $\beta$ -spodumene, potassium dihydrogen orthophosphate and anhydrous potassium hydroxide, most preferably hydrated hydrogen uranyl phosphate.

- Preferably the reference electrode (ii) is one of  $\text{MnO}_2/\text{MnO.OH}$ , tungsten/defect hydrogen tungsten bronze, and the molybdenum and iridium analogues thereof; of these, tungsten/defect hydrogen tungsten bronze is preferred, and is preferably made by electrolytically anodising tungsten, preferably until, at a constant applied voltage (preferably 70V–90V), the anodising current falls to a steady level, and equilibrating the anodised tungsten with the electrolyte.

- A known reference electrode (Solid State Ionics, 7(1982)53–56) comprises palladium or platinum powder continuously contacted with wet hydrogen gas from an external supply, which must be transported always with the probe and the partial pressure of the hydrogen from which must be continuously monitored.

- Preferably the conductive component (i) is a noble metal in which hydrogen is soluble and mobile (noble for resisting attack by the electrolyte) such as palladium or its alloys, such as palladium containing 0 to 40 weight per cent silver. Where the hydrogen concentration in a metal is to be measured, the component (i) is preferably applied as a coherent coating

on the metal.

- The invention also provides a method of measuring the concentration of hydrogen, comprising exposing the conductive component of a hydrogen concentration meter as set forth above to the hydrogen (whether in a solid (e.g. a metal), liquid or gas (e.g. air)) to be measured, and measuring the voltage generated between the conductive component and the reference electrode.

- A by-product of metallic corrosion is commonly the production of hydrogen gas. Therefore, as one application, the invention provides a method of detecting or measuring corrosion of a metal, comprising measuring the concentration of hydrogen in it by the method set forth above. Excessively strong cathodic protection of a metal component can also cause hydrogen to be produced on the metal. In another application, therefore, the invention provides a method of detecting excessive cathodic protection of a metal, comprising measuring the concentration of hydrogen in it by the method set forth above.
- 90 During electroplating, hydrogen may be co-deposited with the metal, and in another application the invention provides a method of detecting hydrogen which has been co-deposited during electroplating, comprising measuring the concentration of hydrogen in the electroplated product by the method set forth above.

- The invention will now be described by way of example with reference to the accompanying drawings, in which

- Figure 1 shows a hydrogen concentration meter which can detect hydrogen in air, and  
 Figure 2 shows a hydrogen concentration meter which can detect hydrogen dissolved in a solid metal.

- In Fig. 1, a generally cylindrical palladium canister 1 (outside diameter 2 mm, wall thickness 0.2 mm) is tightly packed with hydrogen uranyl phosphate as a solid-state electrolyte 2 for conducting hydrogen ions. An axial reference electrode 3 of anodised tungsten wire (about 300 mm long) contacts the electrolyte 2 through a hermetic seal 4 for the canister. A voltmeter V measures the potential between the canister 1 and the reference electrode 3. In this way it is possible to overcome the dehydration problems reported (ibid).

- If hydrogen is present in the air, it will dissolve and diffuse into the palladium canister 1, reversibly forming a solid solution of palladium and hydrogen. Although reversible, the solid solution forms in minutes but evolves hydrogen over (typically) 10 to 20 hours. When the hydrogen concentration exceeds about 1 atomic per cent,  $\text{PdH}_2$  becomes stable, that is,  $\beta$ -phase palladium hydride is liable to be nucleated, and hence reversion to Pd when hydrogen is removed becomes even more sluggish, i.e. days or weeks. This effect may be useful if the hydrogen concentration

meter is needed to detect whether high concentrations (1 per cent or more) of hydrogen have at any time been present, the meter being checked perhaps once a week. If this

- 5 slow reversion of  $\text{PdH}_2$  is however unacceptable, the palladium may be alloyed with silver; the more silver, the higher the hydrogen concentration which the alloy can contain without forming the rather stable hydride, until at 40% silver, the alloy can tolerate a greater level of hydrogen without forming the rather stable hydride.

- The thicker the gauge of palladium used to make the canister, the slower the response but the greater the robustness of the meter. Palladium (and its alloys) are preferred as having a high hydrogen solubility and diffusivity and hence giving a fast response, while also resisting the corrosive effect (to be explained) of the electrolyte 2.

- The solid-state electrolyte is hydrogen uranyl phosphate  $\text{H}(\text{UO}_2)_2\text{PO}_4 \cdot n\text{H}_2\text{O}$  ( $n=4$ ), compressed dry in the canister under mild heat (30–40°C) under 5 MPa until densification stops (about 30 minutes). Alternatively, hydrogen uranyl arsenate or hydrogen uranyl periodate, with the hydrogen optionally partly substituted by other cations, may be used, all as described in British Patent Specification 1571116.

- The reference electrode 3 is tungsten or tungsten-coated wire, coated with tungsten oxide  $\text{WO}_3$  by slurry coating, vapour deposition or, in this case, anodising. It must be a material which will withstand the corrosive effect of the solid-state electrolyte 2, which, if hydrogen uranyl phosphate tetrahydrate, is equivalent to 12M acid. Thus, apart from tungsten, anodised molybdenum and iridium would be suitable.

- For best results, the anodising of the tungsten is not left to chance but is performed thus:

- The tungsten wire to be anodised is dipped into a 10% solution of sulphuric acid, together with a counterelectrode of platinum. A gradual increasing DC voltage is applied between the tungsten (anode; +ve) and the counterelectrode (cathode; -ve), to cause a current not exceeding 20 mA to flow until the voltage equals 80V. The voltage is maintained until the current ceases to decay (it levels off at about 6 mA), which takes about 1 minute, some oxygen and some hydrogen being evolved. The tungsten wire, which may for simplicity be regarded as W coated with  $\text{WO}_3$  (tungsten oxide being a 'defect' compound), is rinsed and dried and allowed to equilibrate in intimate contact with hydrogen uranyl phosphate (HUP), conveniently by packing the HUP around the wire in the canister; thus assembly of the meter will cause the desired equilibration (to a defect hydrogen tungsten bronze  $\text{H}_x\text{WO}_3$ ) automatically, if the meter is not put to use immediately but is left for 12

to 48 hours.

- The voltmeter V can be connected to electronic hardware to show directly the hydrogen concentration; the reproducibility is well within 10% and can reach 2%. The limit of detection is about  $\frac{1}{2}$  parts per million. A typical rest potential in air of a freshly equilibrated meter is about -150 to -200 mV, but after the first exposure to significant (100 ppm) hydrogen, the rest potential in air becomes more reproducible, at -160 mV  $\pm$  10 mV, which is maintained for (at least) many months. In some cases, the reference electrode had to be electrolytically charged with hydrogen by passing a small current through the electrode to the reference electrode, in order to reach this level of reproducibility. Even without that precaution the voltage change registered by the voltmeter V on exposure of the canister 1 to standard conditions of hydrogen is the same for all meters made this way.

- The voltmeter V cannot itself show hydrogen concentration directly, since the response of the meter is diffusion-controlled, but on a step exposure to two concentrations of hydrogen, the two rates of change of recorded voltage at the instant of exposure are believed to be in proportion to the respective concentrations, using which effect a dedicated microchip could be attached to the voltmeter V to give direct readings in units of hydrogen concentration.

- Turning to Fig. 2, a hydrogen meter according to the invention is shown complete (on the left-hand side) and under construction (on the right-hand side) for detecting the hydrogen concentration in a steel member 10 such as an oil pipeline. An excessively strongly cathodically protected pipeline will evolve hydrogen on its surface, leading to embrittlement which can be as catastrophic as the corrosion which has been prevented.

- A coherent coating 11 of palladium is applied to an accessible area of the steel member 10, by vapour deposition, electrolytic plating, electroless plating or explosive forming of a palladium sheet onto the area. Electroless plating from a hypophosphite bath has proved suitable, for example using a bath of the following composition:

$\text{PdCl}_2$	2 g dm <sup>-3</sup>
HCl (38%)	4 ml dm <sup>-3</sup>
120 $\text{NH}_3$ (28%)	160 ml dm <sup>-3</sup>
$\text{NH}_4\text{Cl}$	27 g dm <sup>-3</sup>
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	10 g dm <sup>-3</sup>

- Stock solution of 20 g dm<sup>-3</sup>  $\text{PdCl}_2$  plus 40 ml dm<sup>-3</sup> HCl (38%) is added to the appropriate quantity of ammonium hydroxide with stirring, stood for 20 hours at room temperature then filtered. Hypophosphite solution is added last and the bath brought up to final volume. The final solution is applied to the

steel member 10 at 55C, and palladium deposits at a rate of  $2.5 \mu\text{m hr}^{-1}$ .

Hydrogen uranyl phosphate as a solid electrolyte 12 is pressed in place over the palladium coating 11, and onto the HUP electrolyte is pressed tungsten oxide as a reference electrode 13.

A voltmeter is connected between the palladium coating 11 on the steel member 10 and the reference electrode 13. According to the hydrogen concentration in the steel member 10, the hydrogen concentration will vary in the palladium coating 11 and so, directly, will the voltage across the electrolyte 12.

A schematic hydrogen concentration meter is shown under construction on the right-hand side of Fig. 2. A coherent palladium coating 11, applied as already described to the steel member 10, has mounted on it a stout ring 15 (internal diameter 12 mm) temporarily sealed around its lower periphery to the coating 11.

Dry powered hydrated hydrogen uranyl phosphate  $\text{H}(\text{UO}_2)_2\text{PO}_4 \cdot n\text{H}_2\text{O}$  (when  $n$  is typically about 4), which may be synthesised as described in UK Specification 1571116, is placed (as 12) to a depth of about 10 mm in the ring 15. A stainless steel piston or ram 14, which is a good fit in the ring 15, is painted with a methanolic slurry of tungsten oxide  $\text{WO}_x$  (nominally  $\text{WO}_3$ ), for forming the reference electrode 13. The ram 14 is pressed home under 50 MPa pressure at 50–60C for about 30 minutes. This appears to effect a sintering together of the tungsten oxide and the hydrogen uranyl phosphate electrolyte 12, and the desired equilibrium between these two materials starts to be reached, whereby a constant hydrogen activity in the reference electrode 13 is afforded.

Instead of the coherent coating 11, a stainless steel gauze may be laid on the steel member 10. A fine sprinkling of any non-corroding metallic powder (for example palladium or platinum) is applied to the lower (as drawn) surface of the hydrogen uranyl phosphate electrolyte 12, which is pressed onto the gauze. The gauze is protected by an O-ring seal compressed between the ring 15 and the steel member 10. Otherwise, the meter is identical to that of Fig. 2. The response of this meter is fast.

If this modified meter is applied not to a member 10 but to an apertured stainless steel disc, with the aperture exposing the gauze, on the far side of which are the sprinkled powder and the electrolyte 12, then this meter will detect hydrogen in air (which is free to circulate through the gauze of the electrolyte 12). If water is allowed to condense on the electrolyte 12, the meter gives a large response (possible representing the hydrogen activity in water), masking the true gaseous ambient hydrogen concentration. A porous membrane, e.g. paper or cloth, placed over the electrolyte

(preventing condensation) overcomes this.

## CLAIMS

1. A hydrogen concentration meter, comprising

(i) a conductive component exposable to the hydrogen to be measured and in which hydrogen is soluble and mobile,

(ii) a reference electrode which can reversibly accept hydrogen, and  
(iii) a solid-state electrolyte for hydrogen cations connecting the component (i) with the reference electrode (ii), the said component and reference electrode being connectable to opposite sides of a voltmeter,

characterised in that the reference electrode (ii) has an inherent hydrogen activity and reaches a hydrogen-concentration equilibrium with the electrolyte (iii).

2. A hydrogen concentration meter according to Claim 1, wherein the electrolyte (iii) is one of phosphomolybdic acid, phosphotungstic acid, zirconium hydrogen phosphate, partially hydrated zirconia, hydrated hydrogen uranyl phosphate/arsenate/periodate, perfluorocarbon sulphonic acid,  $\beta$ -alumina (which may be hydronium-substituted), hydrogen- $\beta$ -spodumene, potassium dihydrogen orthophosphate and anhydrous potassium hydroxide.

3. A hydrogen concentration meter according to Claim 2, wherein the electrolyte (iii) is hydrated hydrogen uranyl phosphate.

4. A hydrogen concentration meter according to any preceding claim, wherein the reference electrode (ii) is one of  $\text{MnO}_2/\text{MnO.OH}$ , tungsten/defect hydrogen tungsten bronze, and the molybdenum and iridium analogues thereof.

5. A hydrogen concentration meter according to Claim 4, wherein the reference electrode (ii) is tungsten/defect hydrogen tungsten bronze.

6. A hydrogen concentration meter according to Claim 5, wherein the reference electrode (ii) has been made by electrolytically anodising tungsten and equilibrating the anodised tungsten with the electrolyte (iii).

7. A hydrogen concentration meter according to Claim 6, wherein the anodising is performed at a constant applied voltage until the anodising current falls to a steady level.

8. A hydrogen concentration meter according to Claim 7, wherein the said constant applied voltage is 70V–90V.

9. A hydrogen concentration meter according to any preceding claim, wherein the conductive component (i) is a noble metal.

10. A hydrogen concentration meter according to Claim 9, wherein the noble metal is palladium or a palladium alloy.

11. A hydrogen concentration meter according to Claim 9 or 10, wherein the noble metal is applied as coherent coating on a metal the hydrogen concentration in which is

to be measured.

12. A hydrogen concentration meter substantially as hereinbefore described with reference to and as shown in Fig. 1 or Fig. 2 of the accompanying drawings.

13. A method of measuring the concentration of hydrogen, comprising exposing the conductive component (i) of a hydrogen concentration meter as claimed in any preceding claim to the hydrogen to be measured, and measuring the voltage generated between the conductive component (i) and the reference electrode (ii).

14. A method of detecting or measuring corrosion of a metal, comprising measuring the concentration of hydrogen in it by a method as claimed in Claim 13.

15. A method of detecting excessive cathodic protection of a metal, comprising measuring the concentration of hydrogen in it by a method as claimed in Claim 13.

16. A method of detecting hydrogen which has been co-deposited during electroplating, comprising measuring the concentration of hydrogen in the electroplated product by a method as claimed in Claim 13.

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Printed for Her Majesty's Stationery Office  
by Burgess & Son (Abingdon) Ltd.—1984.  
Published at The Patent Office, 25 Southampton Buildings,  
London, WC2A 1AY, from which copies may be obtained.